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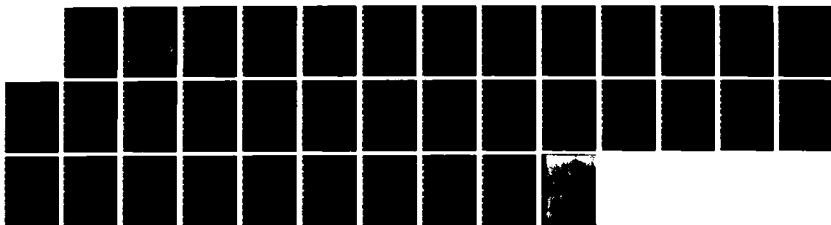
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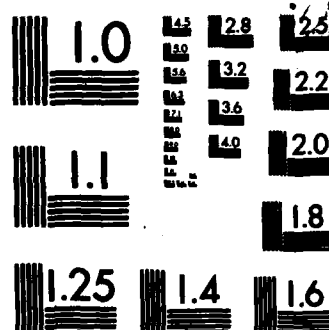
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Films on Electrode Surfaces

by

Marilyn N. Szentirmay and Charles R. Martin

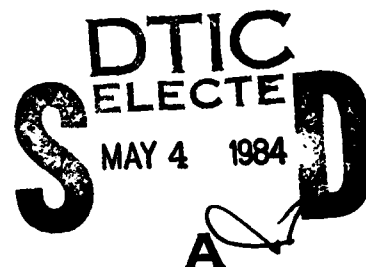
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**ION EXCHANGE SELECTIVITY OF NAFION FILMS
ON ELECTRODE SURFACES**

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Brief

Selectivity coefficients (vs. Na^+) for various electroactive cations were found to be very large, ranging from 1×10^4 to 6×10^6 .

Abstract

Films of 1100 EW Nafion were coated onto glassy carbon electrode surfaces and these chemically modified electrodes were used to characterize the ion exchange selectivity of the polymer. This was accomplished by allowing electrodes to equilibrate with solutions of various electroactive counterions and then determining the quantity of ion incorporated into the films coulometrically. These data were used to calculate both ion exchange partition and selectivity coefficients. Ion exchange selectivity coefficients (vs. Na^+) for hydrophobic, organic counterions were very large (1×10^4 to 6×10^6) confirming earlier work which suggested that Nafion preferentially incorporates such counterions. The implications of this unusual ion exchange selectivity to electroanalysis are discussed.

Introduction

DuPont's Nafion ionomers (1) are proving to be interesting and useful materials for a wide variety of electrochemical applications(2-5). Because of their tremendous versatility, much current research effort is being devoted to studying the morphology, transport properties and mechanical characteristics (1-5) of these polymers. However, very little work aimed at characterizing the ion exchange properties of Nafion has been reported. This is surprising because all applications of Nafion rely on its ability to act as an ion exchange material.

Kirkland prepared Nafion-modified silica particles and used these particles to accomplish high performance liquid chromatographic separations of various cations (6). A low equivalent weight (EW) form (7-9) of Nafion was used and no quantitative studies of the ion exchange properties of this low EW Nafion were reported (i.e., ion exchange selectivity coefficients were not determined and the inherent ion exchange properties of the polymer were not probed). Yeager and Steck (10,11) examined the ion exchange properties of a commercially available, higher EW Nafion; however, only inorganic ions were studied. No general, quantitative study of ion exchange reactions of organic cations in Nafion films or membranes has, to date, been reported.

There is ample evidence which suggests that Nafion (both as thin films and bulk membranes) shows remarkable affinity for hydrophobic cations (7-9, 12-14). Martin and Freiser studied the potentiometric selectivity of 1200 EW Nafion-based ion-selective electrodes (12). These electrodes showed marked preferences for hydrophobic quaternary ammonium cations over simple, inorganic cations (12). Bard, et al. (7,8) and others (9,13) have found that Nafion-based chemically modified electrodes also preferentially incor-

porate certain organic counterions; however, except for one reported ion exchange partition coefficient (7) (see Conclusions section) quantitative data is lacking. Finally, we have recently reported results of luminescence probe studies (14) of the solutions obtained upon dissolving (15) the high EW Nafion polymers. These studies showed that these polymers can engage in strong hydrophobic interactions with organic cations and that because of these interactions, hydrophobic organic cations are preferentially incorporated into the microdomain around the polymer chains (14).

Because of the dearth of quantitative data, we have used an electrochemical method (16) to obtain ion exchange selectivity coefficients for a variety of electroactive counterions at Nafion-based chemically modified electrodes. A commercially available (and technologically more interesting) high EW version of Nafion was used. We report the results of these studies here.

Experimental Section

Materials and Equipment. Nafion (1100 equivalent weight) was generously donated by E.I. Dupont de Nemours & Co. and was dissolved (15) in 50:50 ethanol-water to give a solution of 0.6 wt/vol %. The equivalent weight was verified by titration of the polymer solution with NaOH. 1,1'-dimethyl-4,4'-bipyridinium dichloride, methyl viologen (MV^{2+}), was obtained from Aldrich. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ ($bpy=2,2'$ -bipyridine) and sodium perchlorate, anhydrous, reagent were obtained from G.F. Smith. Ferrocenylmethyl trimethylammonium hexafluorophosphate (FA^+) was prepared from the iodide salt (Pfaltz & Bauer) using aqueous $NaPF_6$ and was recrystallized from water. $Ru(NH_3)_6Cl_3$ was obtained from Johnson Matthey. Glassy carbon rods were obtained from Atomergic Chemetals.

Because of the very large values of the ion exchange selectivity coefficients obtained were, very dilute solutions of the electroactive ions were required. Special care was taken in the preparation of these very dilute solutions. All glassware was cleaned with 50:50 HNO_3 -water and rinsed with copious quantities of triply distilled water. Fresh triply distilled water was used to prepare all solutions. Volumetric flasks were preconditioned prior to use by storing a solution of the desired ion (having the same concentration as the solution to be ultimately prepared) in the flask. Once preconditioned in this way, a flask was used to make solutions of only that electroactive ion at only that concentration level. Fresh solutions were prepared each day.

Electrochemical measurements were carried out in N_2 -degassed solutions using a three electrode cell with a saturated calomel reference electrode (SCE) and a Pt flag counter electrode. A PAR model 173 potentiostat and Model 175 programmer (EG & G PAR) and an X-Y recorder (Houston Instruments) were employed. In an effort to enhance the rates of equilibration, a Pine Instruments model ASR2 rotator was used to rotate the film-coated electrodes in the equilibration solutions. Rotation rates of 1500-2500 rpm were employed.

Procedures. Glassy carbon electrodes were polished and coated with Nafion as previously described (13). The Nafion films were converted to the Na^+ form prior to use by soaking at least 6 hr in 0.1M NaClO_4 . Thicknesses of wet, Na^+ form Nafion films were measured using an Alpha-step surface profiler (Tencor Instruments) or were calculated using 1.58 g cm^{-3} as the wet, Na^+ form density (17). While the films examined with the profilometer showed that the film surfaces were not flat, the average measured thickness always agreed to within better than 10% of the calculated thickness.

The experimental procedure used was similar to that of Schneider and Murray (16). Nafion films on electrode surfaces were equilibrated with dilute (ca. 1×10^{-9} to 3×10^{-7} M) solutions of the electroactive cations in 0.100M NaClO₄. The equilibrium quantity of an electroactive cation in a film was then determined by stepping the potential from a value where no redox reaction occurs to a value well beyond the E° for the cation and monitoring the charge required to quantitatively oxidize or reduce the cation (all redox reactions were one electron reactions). The electrode was stationary during charge measurement. Prior to equilibration, identical potential steps were made in solutions containing only supporting electrolyte so that charge associated with background processes could be measured. The background charge was subtracted from the charge measured at the equilibrated electrode.

The equilibrations were carried out using large volumes of solution (usually 500 mL) in order to avoid appreciably depleting the solution of electroactive cation. The reported equilibrium solution concentrations are corrected for the (small) amount of cation incorporated into the film. Charge was measured with the electrode immersed in the fully equilibrated solutions, since the low concentrations of electroactive species in solution did not contribute appreciably to the coulometric measurement of the Nafion-incorporated ion (18). All experiments were carried out at room temperature ($23 \pm 2^\circ\text{C}$).

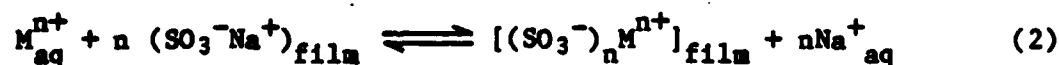
Both 1 μm and 2 μm thick films were used in these experiments, the thicker films being used in order to obtain more accurate coulometric measurements when the concentration of electroactive species in the film was very low. Except for the increased accuracy and somewhat longer equilibration times, there were no differences in results between the 1 and 2 μm films.

An ion exchange selectivity coefficient was measured for $\text{Ru}(\text{bpy})_3^{2+}$ (vs. Na^+) for a conventional ion exchange resin (Dowex 50-X8). The moles of exchange sites per gram dry resin were determined via titration with NaOH . Ca. 0.3 g quantities of the resin were equilibrated, by shaking for one week, with solutions 10^{-3}M in $\text{Ru}(\text{bpy})_3^{2+}$ and 0.1M in NaCl . The equilibrium aqueous concentrations of $\text{Ru}(\text{bpy})_3^{2+}$ were determined spectrophotometrically. These values and the exchange capacity were used to calculate $K_{\text{Na}^+}^{\text{Ru}(\text{bpy})_3^{2+}}$.

Calculations. We express the extent of the exchange of the electro-active cation (M^{n+}) for Na^+ in the Nafion film both in terms of a distribution coefficient, k_D , and an ion exchange selectivity coefficient, $K_{\text{Na}^+}^{\text{M}^{n+}}$. As we shall see, each notation has its useful features. The k_D is the equilibrium coefficient for the hypothetical (vide infra) partition reaction



and is given by $k_D = [\text{M}^{n+}]_{\text{film}}/[\text{M}^{n+}]_{\text{aq}}$. The distribution coefficient is also the slope of the partition isotherm (see Figure 3). $K_{\text{Na}^+}^{\text{M}^{n+}}$ is the equilibrium coefficient for the ion exchange reaction



and is given by (10)

$$K_{\text{Na}^+}^{\text{M}^{n+}} = \frac{\chi_{\text{M}^{n+}}^n a_{\text{Na}^+}^n}{\chi_{\text{Na}^+}^n a_{\text{M}^{n+}}} \quad (3)$$

where the a 's are activities in aqueous solution and the χ 's are the equivalent ionic fractions of $-\text{SO}_3^-$ sites occupied by each ion.

The film concentrations were calculated from the corrected charge values and the known film volumes. The χ values were calculated from the corrected charge values and the known total moles of $-\text{SO}_3^-$ sites in the films. The aqueous ion size parameters used to calculate activities were estimated from ion size data for similar compounds. (19-21). The values used were 4×10^{-8} cm for $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$, 12×10^{-8} cm for $\text{Ru}(\text{bpy})_3^{2+}$ and 8×10^{-8} cm for the other electroactive cations.

Results and Discussion

In order to obtain ion exchange data, it was first necessary to determine the time required for each ion to reach exchange equilibrium with the Nafion-coated electrode. Although the exchange equilibrium between Nafion and water is rapid for small cations (e.g., H^+ and the alkali metal ions (22)), the larger ions studied here exchanged slowly and required longer equilibration times. For example, Figure 1 shows the charge needed to completely reduce all the MV^{2+} incorporated into a Nafion film at various times after immersion of the Nafion-coated electrode into the MV^{2+} solution. It can be seen that at least 12 hr are needed for MV^{2+} to equilibrate with the Nafion film. $\text{Ru}(\text{NH}_3)_6^{3+}$ and FA^+ require about a day to reach equilibrium with a 1 μm film, while $\text{Ru}(\text{bpy})_3^{2+}$ requires about a week. The slow attainment of equilibrium for these cations is a result of the very low concentrations of exchanging ions used and their low ionic diffusion coefficients in Nafion. $\text{Ru}(\text{bpy})_3^{2+}$, in particular, has an extremely low ionic diffusion coefficient in Nafion (estimated to be ca. 10^{-12} $\text{cm}^2 \text{ s}^{-1}$ (13)). The other ions studied here have larger ionic diffusion coefficients in Nafion (1×10^{-10} - 25×10^{-10} $\text{cm}^2 \text{ s}^{-1}$ (13)), but still diffuse

much more slowly than, for example, Na^+ , which has a D of $9.44 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ in Nafion (23)).

Figure 2 shows voltammograms for Nafion-coated electrodes after equilibration with very dilute solutions of the various electroactive counterions. These voltammograms are the first indicators of the magnitudes of the ion exchange selectivity coefficients for these electroactive counterions. No signals above background currents would be detected at uncoated electrodes in these extremely dilute (less than $5 \times 10^{-8} \text{ M}$) solutions. Clearly, the equilibrium film concentrations are orders of magnitudes higher than the solution concentrations.

Ion exchange reactions should be described by an equilibrium coefficient expression, like that shown in equation 3, which takes into account the solution and film concentrations of both the exchanging and exchanged ions. However, when the concentration of the exchanged ion (Na^+) in the aqueous phase is high and the concentration of the exchanging ion (M^{n+}) in the film is very low, the a_{Na^+} and χ_{Na^+} terms in equation 3 are constant and the reaction may be regarded as a partition reaction (equation 1) (24,25). Simplifying the ion exchange reaction to a partition reaction is attractive because the extent of the reaction may be conveniently visualized by plotting a partition isotherm ($[\text{M}^{n+}]_{\text{film}}$ vs. $[\text{M}^{n+}]_{\text{aq}}$) (7,16).

Figure 3 shows partition isotherms for the various electroactive cations studied here. The linear portions of these isotherms show the (low) concentration regions over which it is appropriate to use equation 1 to describe the ion exchange process. The slopes of these isotherms, k_D 's, are shown in column 2 of Table 1. The immenseness of these slopes clearly shows that Nafion greatly prefers these electroactive counterions over Na^+ .

As will be discussed below, the slopes or k_D 's are essentially Nafion/water preconcentration factors and the immense sizes of these k_D 's suggest that Nafion would be a useful preconcentration material for these or similar ions (8).

While the partition isotherm allows for a convenient visualization of the extent of the ion exchange reaction, if ion exchange data obtained here are to be compared with existing data for these or other ion exchange systems, and if the data outside of the linear isotherm region are to be treated, ion exchange selectivity coefficients (equation 3) should be calculated. Ion exchange selectivity coefficients for the various electroactive counterions are shown in column 3 of Table 1. These coefficients were calculated from points on both the linear and non-linear portions of the isotherms; equivalent ionic fractions as high as 0.4 were used. While, as indicated by the standard deviations, there is some scatter in these coefficients, no trends in $K_{Na^+}^{Mn^+}$ with χ_{Mn^+} were observed.

The magnitudes of these ion exchange selectivity coefficients are truly remarkable. Yeager and Steck studied exchange reactions of alkali metal and alkaline earth ions in Nafion (10,11). (While these authors used H^+ as the exchanged ion and we used Na^+ , they have shown that $K_{H^+}^{Na^+}$ is about unity (10); this allows for rough comparisons of their coefficients with ours.) The largest selectivity coefficient for a monovalent ion observed by Yeager and Steck was $K_{H^+}^{Cs^+}$, which has a value of 9.1 (10) the largest for a divalent ion was $K_{H^+}^{Ba^{2+}}$, which had a value of about 30 (11). Selectivity coefficients for the ions studied here are from 3 to 6 orders of magnitude larger than these values; clearly, Nafion shows tremendous preference for the ions studied here over the simple inorganic ions studied by Yeager, et al.

Conventional cation exchange materials (i.e., sulfonated styrene-divinylbenzene resins) show ion exchange selectivity coefficients for the alkali and alkaline earth ions of the same order of magnitude as those for Nafion (i.e., 1 to 10) (26). However, since most of the ions studied here are hydrophobic organic cations, it is of interest to compare the ion exchange data obtained here with selectivity coefficients for organic ions on conventional ion exchange resins. Gregor and Bregman studied ion exchange reactions of a variety of alkyl and phenylalkylammonium ions on resins containing from about 1 to 35% divinylbenzene (27). While selectivity coefficients as large as about 15 were observed (27), none of the resins showed the remarkably large ion exchange selectivity coefficients exhibited by Nafion. To allow for more direct comparison, we have determined $K_{Na}^{Ru(bpy)_3^{2+}}$ for a conventional ion exchange resin (Dowex 50X-8); a value of 31 was obtained ($X_{Ru(bpy)_3^{2+}} = 0.12$).

Neglecting, for the moment, $Ru(NH_3)_6^{3+}$, all of the ions studied here are hydrophobic, organic cations. Hence, the data obtained here corroborate the conclusion reached by Martin and Freiser (from ion-selective electrode data) that Nafion shows tremendous affinity for hydrophobic cations (12). This conclusion is also corroborated by our luminescence probe studies of Nafion polyelectrolyte in solution (14) and our very recent investigations of Nafion based high performance liquid chromatography (HPLC) columns (28).

Conventional ion exchange materials do not show this marked preference for hydrophobic counterions (27). We believe that the difference between the exchange characteristics of Nafion and conventional resins can be explained by considering the structural differences between these polymers. First, conventional ion exchange resins are covalently cross-linked, while

Nafion is not. The Gibbs-Donnan equation (the fundamental thermodynamic equation for exchange reactions (29)) accounts for the effect of cross-linking through inclusion of a PV term (29). This term discriminates against ions of large size (large V) (27,29). Since Nafion is not cross-linked, there should be no PV-based discrimination against large ions, and, therefore, large ions may be partitioned into Nafion without the thermodynamic penalty inherent in the Gibbs-Donnan equation (30).

The second important structural difference between Nafion and conventional ion-exchange resins is that in Nafion, only about 1 in every 8 monomer units is sulfonated, while conventional resins are close to 100% sulfonated. We believe that the large segments of uncharged chain material allow for a greater extent of hydrophobic interaction and that it is these hydrophobic interactions which drive ion exchange reactions for organic cations in Nafion.

Our various studies (13,14,28) of Nafion provide ample evidence for the importance of hydrophobic interactions. $\text{Ru}(\text{NH}_3)_6^{3+}$ is not, however, a hydrophobic ion, yet $K_{\text{Na}}^{\text{Ru}(\text{NH}_3)_6^{3+}}$ is very large. It seems likely that the enhanced electrostatic interaction might be partially responsible for the strong affinity Nafion shows for $\text{Ru}(\text{NH}_3)_6^{3+}$. This suggestion is supported by the fact that calculated (31) E° values shift from -0.173 V vs. SCE in solution (0.1 M NaClO_4) to about -0.293 V vs. SCE in the Nafion film. With this potential shift and the measured k_D for $\text{Ru}(\text{NH}_3)_6^{3+}$ a k_D for $\text{Ru}(\text{NH}_3)_6^{2+}$ can be calculated (32). The calculated k_D for $\text{Ru}(\text{NH}_3)_6^{2+}$ is two orders of magnitude lower than k_D for $\text{Ru}(\text{NH}_3)_6^{3+}$ (see Table 1). This dramatic decrease in the partition coefficient upon decreasing the charge of the ion clearly shows that electrostatic interactions are, indeed, important in the binding of $\text{Ru}(\text{NH}_3)_6^{3+}$ to Nafion.

There are, however, two bits of evidence which strongly suggest that the enhanced electrostatic interaction is not the only factor responsible for the strong binding of $\text{Ru}(\text{NH}_3)_6^{3+}$ to Nafion. First, we have found that Nafion has very little affinity for other trivalent ions (e.g., Fe^{3+} , Eu^{3+}). For example, while Fe^{3+} is taken up by Nafion films, only trace amounts of the metal are retained when the electrodes are transferred to a solution containing only supporting electrolyte, as evidenced by the nearly complete disappearance of the $\text{Fe}^{3+/2+}$ voltammetric wave. (To minimize hydrolysis and complexation effects, 0.25 M HClO_4 was used as the supporting electrolyte for these studies.) Second, not only is $K_{\text{Na}^+}^{\text{Ru}(\text{NH}_3)_6^{3+}}$ very large but, considering the fact that hydrophobic interactions should not be important, the selectivity coefficient for the divalent form of the complex is also abnormally large; $K_{\text{Na}^+}^{\text{Ru}(\text{NH}_3)_6^{2+}}$ is over an order of magnitude larger than the largest reported selectivity coefficient for a divalent ion (11) (see Table 1). The lack of affinity of Nafion for other trivalent ions and the strong affinity of Nafion for $\text{Ru}(\text{NH}_3)_6^{2+}$ suggests that there is something unique about the interaction between Nafion and the rutheniumhexamine. This unique factor remains to be elucidated.

Oyama and Anson (33) and Martin, et al. (8) have suggested the possibility of using ion exchange polymer films on electrode surfaces to preconcentrate counterions prior to electroanalysis. The partition isotherms shown in Figure 3 confirm this possibility and show that the preconcentration advantage is immense. However, the very long equilibration times (Figure 1) would prohibit realization of the full preconcentration advantage. If a chemically modified electrode of this type were to be used for chemical analysis, a compromise between detection limit (as determined by the extent of the partition reaction) and time of analysis would have to be reached.

We are beginning to investigate this detection limit vs. time trade-off. A Nafion film modified electrode was immersed in a solution 0.2M in sodium trifluoroacetate (TFA) and a background linear sweep voltammogram (100 mV s^{-1}) was obtained. The electrode was then stirred for 20 min. in a solution 10^{-8} M in methylviologen and 0.2 M in TFA (the "analyte" solution) after which the electrode was transferred to the TFA solution and a voltammogram obtained. This was repeated for several concentrations of MV^{2+} . A calibration curve of cathodic peak current vs. concentration of MV^{2+} in the "analyte solution" was plotted from these data. This calibration curve is beautifully linear (correlation coefficient = 0.9999) over the concentration range studied (10^{-8} to 10^{-6} M). Furthermore, even though the film was immersed in the analyte solution for only a very small fraction of the time required to reach equilibrium, the detection limit for MV^{2+} (2 times signal to background) is 10^{-8} M ; this is about 3 orders of magnitude lower than the detection limit observed for linear sweep voltammetry at a comparable uncoated electrode, but much higher than the theoretically possible detection limit had the film been allowed to reach equilibrium with each solution. Obviously, much further work, including attempts to identify polymers with faster mass transport rates, studies of the effect of waveform (e.g. sweep, pulse, differential pulse, etc.) on detection limit, studies of effect of film thickness, etc., will be required before conclusions concerning the analytical utility of ion exchange polymer-modified electrodes can be reached.

Conclusions

Ion exchange selectivity coefficients (vs. Na^+) for various electroactive, organic cations at Nafion films on electrode surfaces have been shown

to range from ca. 1×10^4 to ca. 6×10^6 . These enormous selectivity coefficients confirm conclusions reached from potentiometric (12) and luminescence probe (14) studies which suggested that Nafion shows tremendous preference for hydrophobic, organic cations. We have proposed a model which attributes this unusual ion exchange selectivity to Nafion's unique structural characteristics. Ensuing papers dealing with HPLC investigations of Nafion (28) and other ionomers will describe further tests of this model. Nafion also strongly binds both $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$. It is not at this point clear why Nafion has such high affinities for these complexes. While from a thermodynamic point of view, Nafion appears to be an ideal polymer for preconcentration of organic cations, the dynamics of its exchange processes may prohibit exploitation in chemical analysis.

Finally, as noted earlier, White et al. (7) determined a k_D for FA^+ at a 970 EW Nafion film on a carbon electrode. Transformation of this k_D into a $K_{\text{Na}^+}^{\text{FA}^+}$ produces a value of about 1×10^3 , 3 orders of magnitude lower than the $K_{\text{Na}^+}^{\text{FA}^+}$ determined here. The most likely explanation for this discrepancy is that the ion exchange characteristics of the 970 EW Nafion are dramatically different from those of the 1100 EW Nafion used here. It is known, for example, that the water content of 970 EW Nafion is much higher than that of 1100 EW Nafion (34); the higher water content of the 970 EW polymer could be responsible for the decreased affinity of this polymer for the very hydrophobic FA^+ .

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Credit

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Table 1. Ion Exchange Partition Coefficients, k_D , and Selectivity

Coefficients $K_{Na^+}^{Mn^+}$.

Cation	k_D	$K_{Na^+}^{Mn^+}$
MV^{2+}	7.9×10^5	$1.5(\pm 0.2) \times 10^4$
FA^+	1.1×10^6	$7.3(\pm 0.9) \times 10^4$
$Ru(NH_3)_6^{3+}$	2.5×10^6	$3.7(\pm 0.5) \times 10^4$
$Ru(bpy)_3^{2+}$	2.1×10^7	$5.7(\pm 1.1) \times 10^6$
$Ru(NH_3)_6^{2+}$, ^a	2.6×10^4	740 , ^b

^a Calculated from $(E_{pa} + E_{pc})/2$ shift. See text.

^b Assuming $\chi_{Na^+} = 0.90$.

Figure Captions

Figure 1.

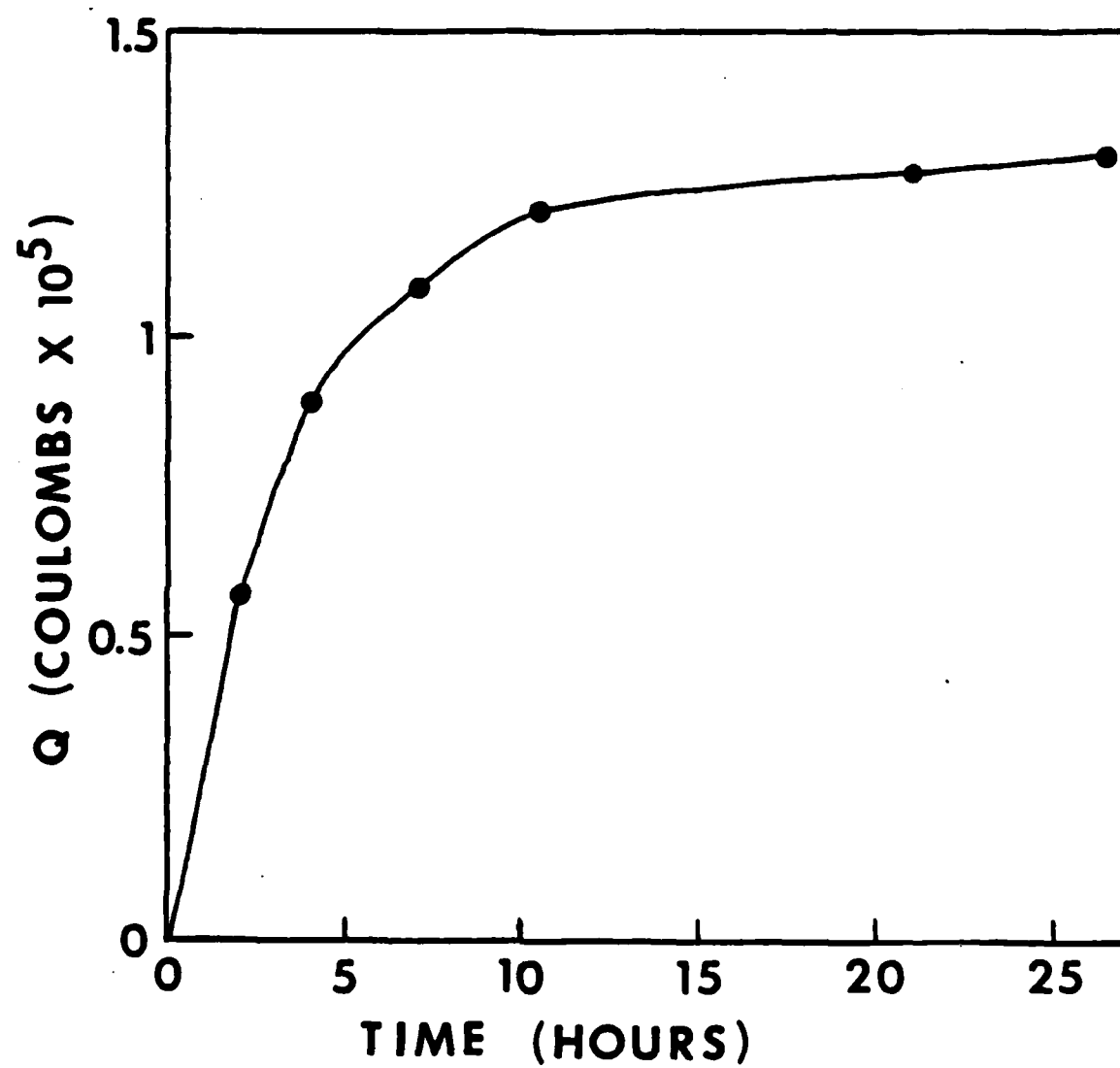
Equilibration of Nafion-coated electrode ($1\mu\text{m}$ thick, 1.1×10^{-8} moles SO_3^- sites, initially in Na^+ form) with 2.32×10^{-8} M MV^{2+} in 0.1 M NaClO_4 . The charge, Q , required to completely reduce MV^{2+} in the Nafion film is measured vs. time after immersion in the MV^{2+} solution. The electrode was spun at 1500-2500 rpm.

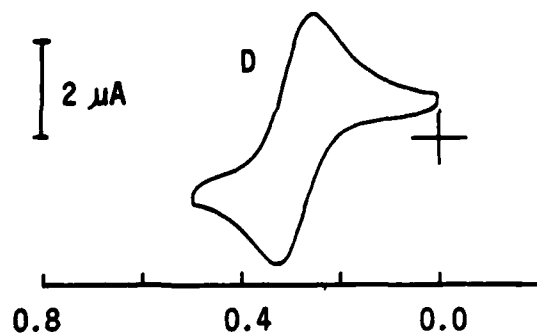
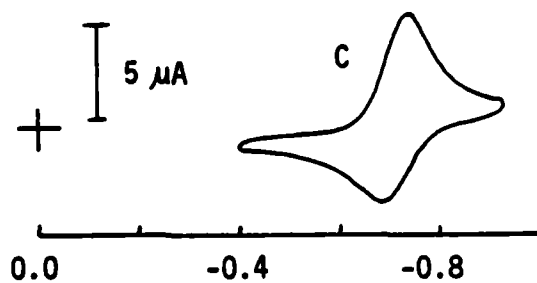
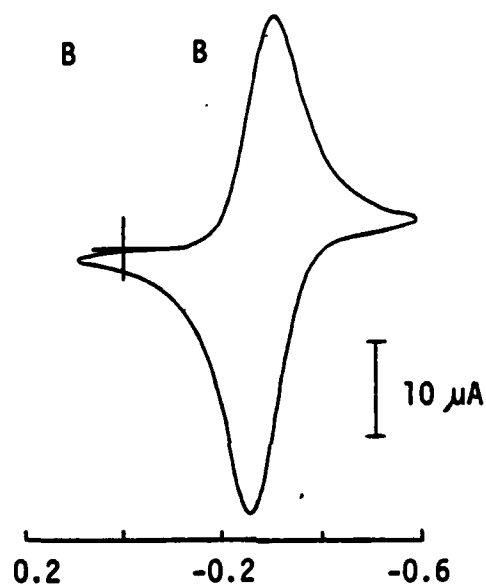
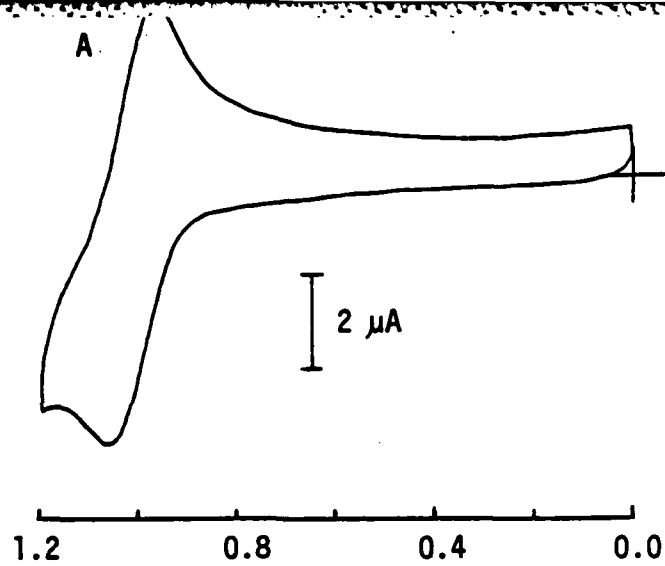
Figure 2.

Cyclic voltammograms recorded at a scan rate of 0.1 V s^{-1} for Nafion-coated electrodes in equilibrium with: A. 1.51×10^{-8} M $\text{Ru}(\text{bpy})_3^{2+}$, B. 2.78×10^{-8} M $\text{Ru}(\text{NH}_3)_6^{3+}$, C. 4.36×10^{-8} M MV^{2+} , D. 3.40×10^{-8} M FA^+ . Supporting electrolyte: 0.100 M NaClO_4 .

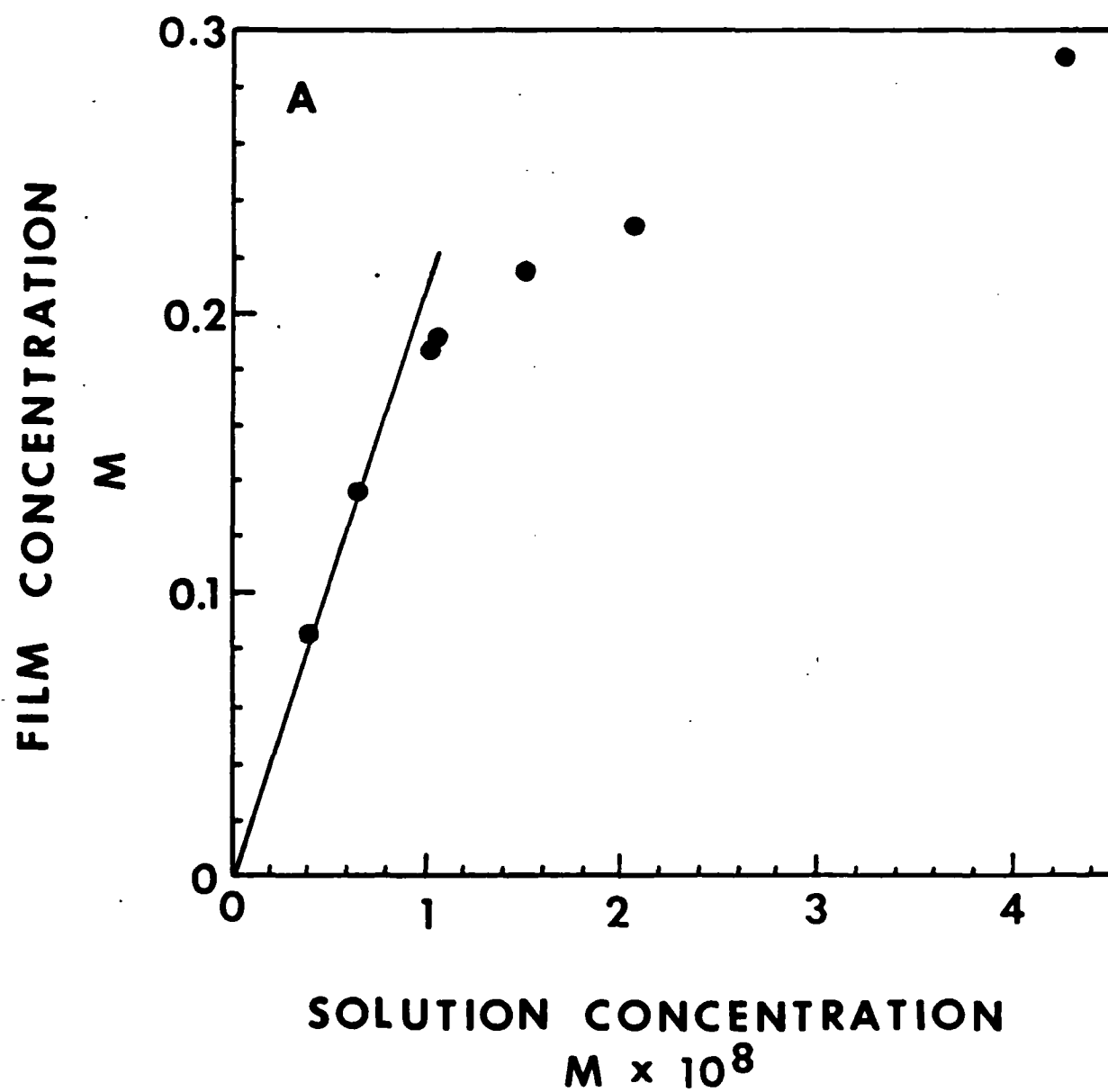
Figure 3.

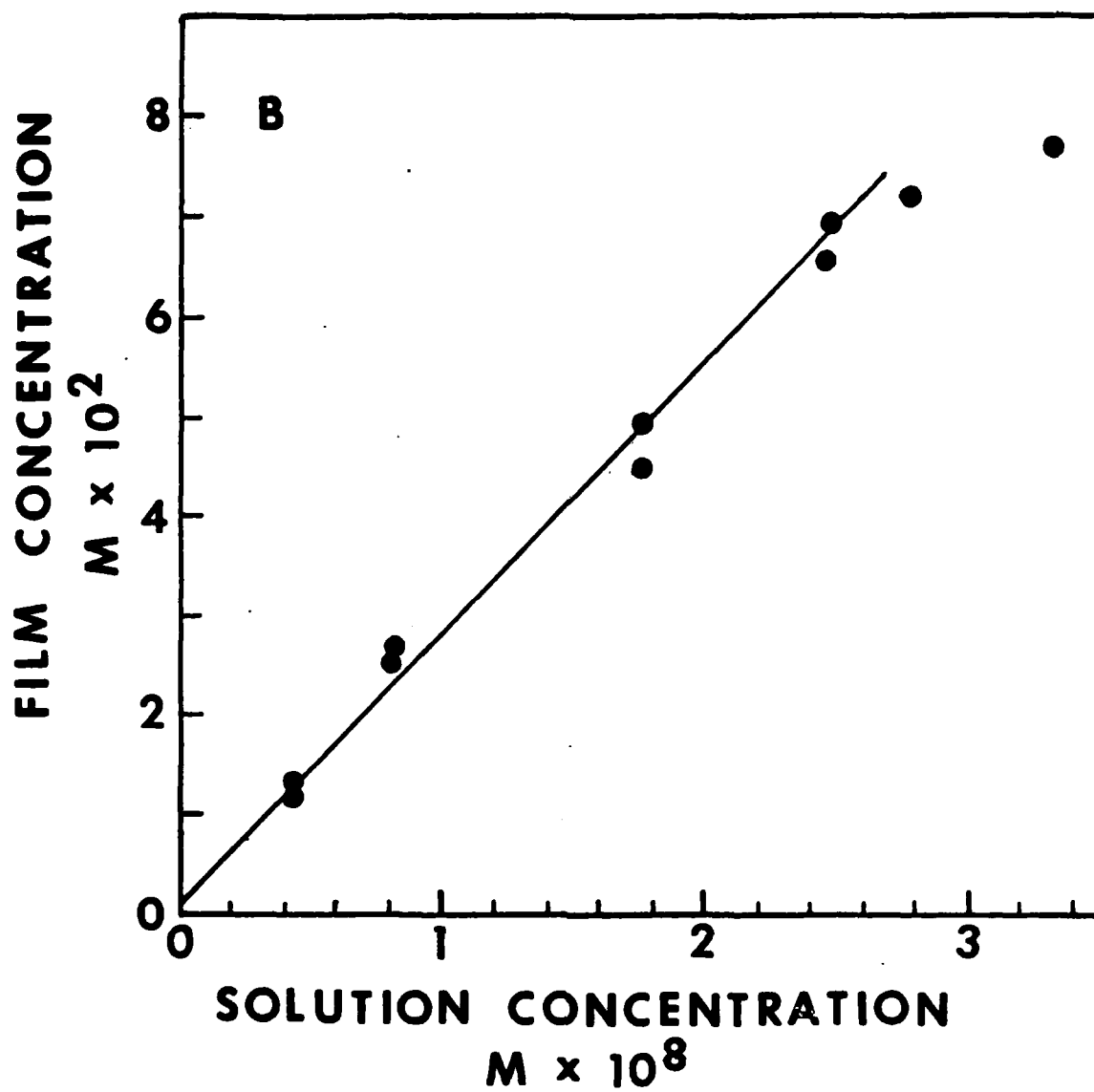
Ion exchange isotherms for Nafion-coated electrodes. A. $\text{Ru}(\text{bpy})_3^{2+}$, B. $\text{Ru}(\text{NH}_3)_6^{3+}$, C. MV^{2+} , D. FA^+ .

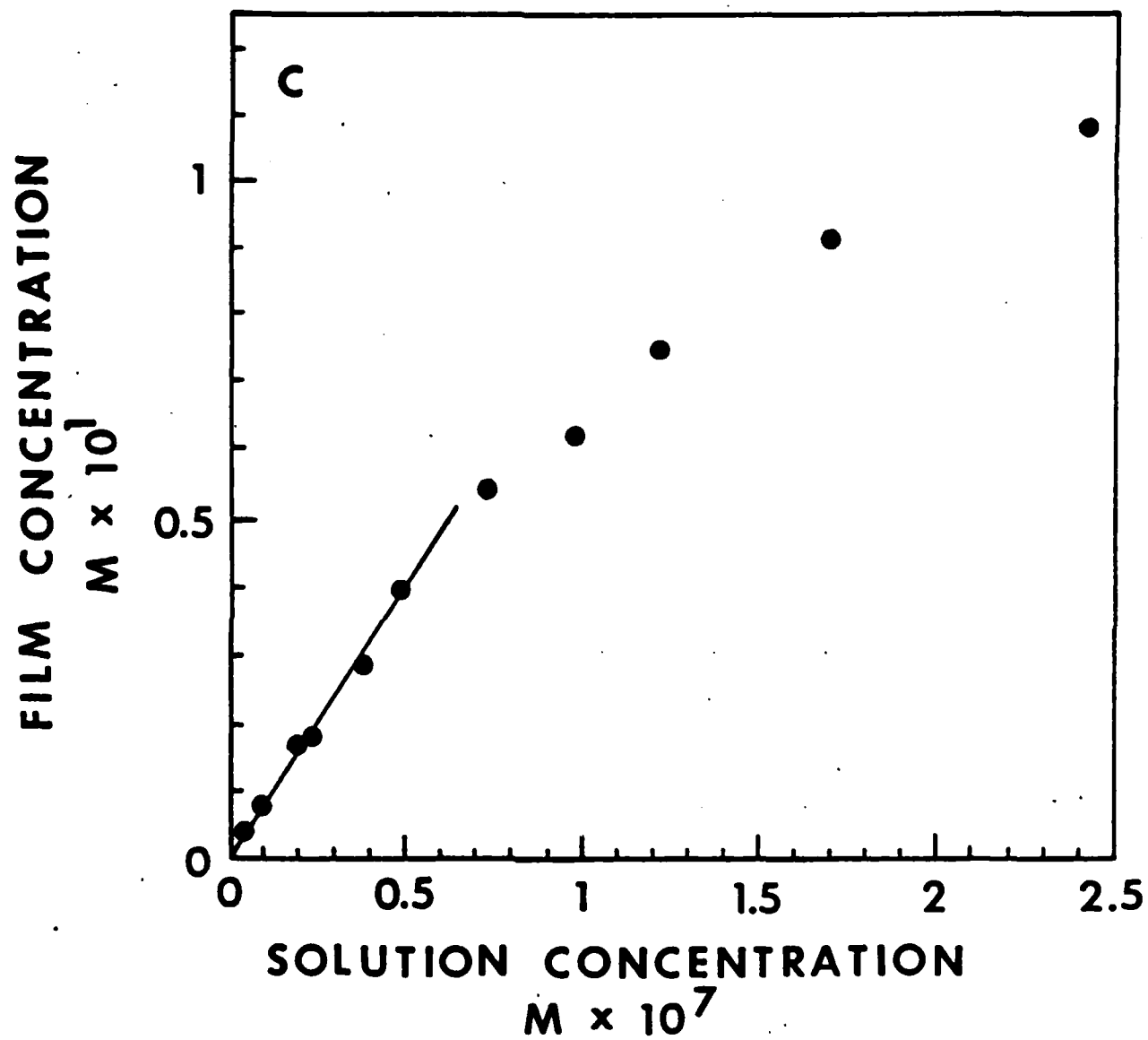


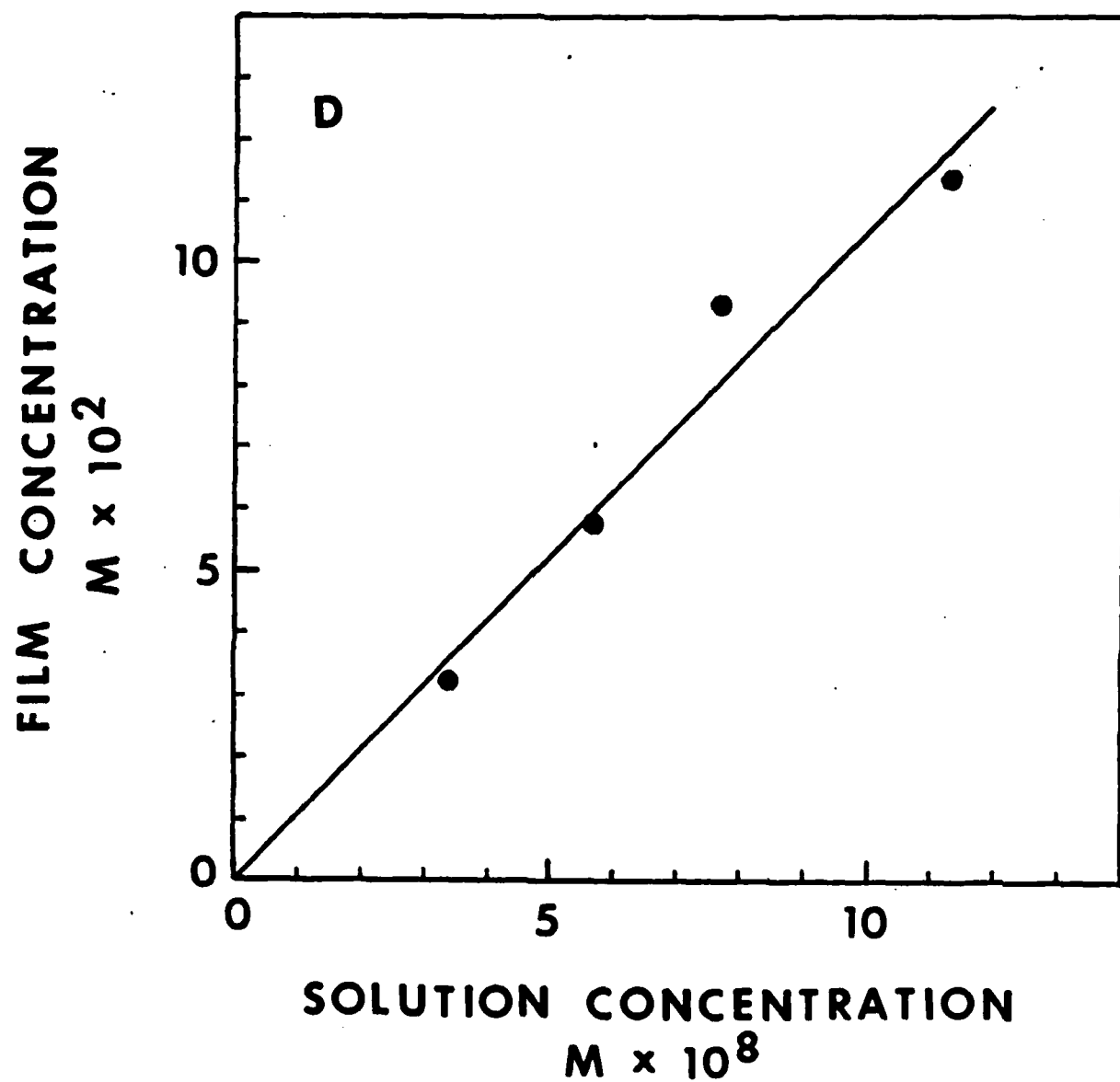


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